Frustrated Magnetism and Searching for Quantum Spin Liquid Phases in Novel Materials

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In my research, I wish to classify and identify a possible Quantum Spin-Liquid (QSL) phase on novel quantum materials. Materials of interest include the two triangular lattice materials, Li_4CoTeO_6 and Li_4NiTeO_6, in which Ni and Co ions with effective spin-1 and spin-1/2 each occupy a triangular lattice. We performed thermodynamic and magnetization measurements which indicate a possible exotic magnetic ground-state in both materials. We then performed elastic neutron scattering, providing additional evidence for exotic magnetism in these materials. Inelastic neutron scattering measurements are still necessary to probe the nature of the magnetic correlations and to confirm a QSL phase. Another material of interest is the kagomé lattice material, $KFe_3(OH)_6(SO_4)_2$ (known as Fe-Jarosite). This material is a popular QSL.[1,2] Small crystals of Fe-Jarosite have been created by hydrothermal synthesis in Mourigal Lab, and preliminary measurements of magnetization are in good agreement with known values.[1,3] Neutron scattering is required to study this material's spin-dynamics, however, scattering is weak. Therefore, further synthesis attempts must be performed in order to increase the size of single-crystals of Fe-Jarosite from 2.6 mm to 1.0 cm.

Introduction

In 1973, Philip Anderson first proposed the existence of the "quantum spin-liquid" (QSL) as a new state of magnetic matter.[4,5] In conventional magnets, electron spins are known to either align parallel or antiparallel (ferromagnetic or antiferromagnetic, Figure 1a and 1b) to their nearest neighbors while the material is below some critical temperature, T_C.[6] This nearest neighbor interaction induces a long-range ordering of electron spins throughout the material: the relative position of spins is fixed, independent of the distance between electrons. The QSL, however, will take an unordered (paramagnetic or diamagnetic) ground state. Even at absolute zero temperature, the electron spins will fluctuate, and long-range order is never achieved. These frustrated spins are a consequence of the geometry, or topology, of the material. Consider, for example, a triangular-lattice with one valence electron on each vertex. Two of the electrons will tend to order with each other, $+1/2$ and -1/2, but the third electron will remain frustrated (Figure 1d). A more complex lattice configuration would be the kagomé lattice (Figure 1e), which has similar geometric features to the triangular-lattice, which attribute to the spin frustration. In the case of the triangular lattice, cooler and cooler temperatures could "freeze" the electron spins of one triangular segment into the ground state with 120-degree order, which then determines the long-range order throughout the rest of the lattice. This material is considered a "spin-solid". In the kagomé lattice, however, freezing the spins of one triangular segment in the lattice does not necessarily determine the order throughout the rest of the material. In fact, there are many degenerate ground states for the kagomé lattice, which cause it to favor spin-liquid states.[6] These states are promising for topologically protected quantum computing.[7]

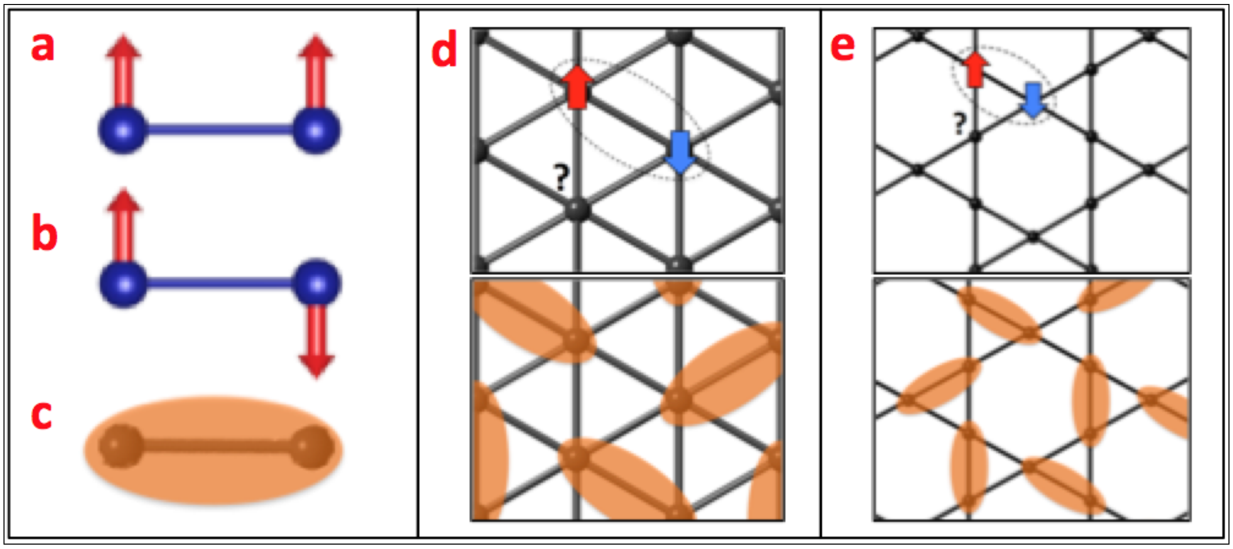

Figure 1: **a)** Spins align ferromagnetically and **b)** antiferromagnetically. **c)** Two electrons may take a superposition of ferromagnetic states but still remain coupled to each other. **d)** Geometric frustration can be seen on the triangular lattice (top), with electrons' spins freezing bellow some temperature, T_C (bottom). **e)** A more complicated structure, the kagomé lattice, exhibits similar frustration (top) and freezing (bottom) as on the triangular lattice.

Thesis Outline

This work is organized in three chapters and an appendix.

Chapter 1 is an introduction to quantum materials research as well as a literature review of relevant work in the field. Technological applications and the motivation for quantum materials research are presented. Existing gaps in our understanding, current technological limitations for experimentation, as well as possibly future advancements in the field are discussed.

Chapter 2 is a report of research performed on two triangular-lattice antiferromagnets (TAFs), Li_4CoTeO_6 and Li_4NiTeO_6. We wish to describe the exotic magnetic properties due to frustration and determine the magnetic ground state of each material. Magnetization, specific heat, and neutron scattering results are presented. These results are discussed in the context the QSL or partial QSL phase and compared with experimental observations for another Li-TAF.

Chapter 3 investigates the popular kagomé lattice material, Fe-Jarosite ($KFe_3(OH)_6(SO_4)_2$). After a brief literature review of previous Fe-Jarosite research, our synthesis, characterization, magnetization and specific heat results are presented. These results are discussed in the context of the QSL phase as well as the importance of topology in materials. Further discussion investigated the topological insulator phase and the possible bridge between two related topics of study: topological insulators and frustrated magnetism.

Chapter 1

Literature Review

1.1 Forward

Condensed matter physics is the study of the physical properties of condensed phases of matter. Particles adhere closely to one another, and various interactions occur: topology, entanglement, and spin-orbit coupling, to name a few. Exotic phases of matter and interesting physical behaviors arise from these competing interactions. Such behaviors can lead to superconducting or topologically protected phases, which have implications for energy harvesting, quantum computing, and many more technological advances outlined by the U.S. Department of Energy in their Basic Research Needs Workshop on Quantum Materials for Energy Relevant Technology.[8] Additionally, the D.O.E. outlines Priority Research Directions (PRDs) in quantum materials and some of the real world applications of this research. There is significant motivating and funding to advance our understand of quantum materials. Therefore, it is the goal of experimental condensed matter physicists to realize these exotic phases in real materials, for the practical purposes of advancing modern technology and remaining competitive in the global economy.[8]

1.2 Quantum Materials

In their paper investigating the physics of quantum materials, Keimer and Moore discuss the properties of a variety of quantum materials including superconductors, graphene, topological insulators, Weyl semimetals, quantum spin liquids, spin ices, and more.[9] Each phase possesses its own unique properties which can be applied to technology in different ways.

A superconductor is a material which has zero internal resistivity, therefore transporting electricity at 100 percent efficiency. This type of material is desirable for energy harvesting and energy transportation, and can greatly reduce the cost of energy for the average person's day-to-day uses.[8] Superconductor phases can be found on a variety of materials, given specific environmental conditions, such as low temperature or high pressure. One of the greatest challenges of condensed matter physicists is to increase the temperature T_C at which these superconducting phases occur to allow for more practical applications of such materials.

Topological insulators are materials which are insulating in the bulk but conducting on the surface due to topological effects. In a two dimensional material, the conducting electrons are found on the edges of the material. Since the edge states are protected from backscattering by a time-reversal symmetry rather than an energy gap, these edge phases are conducting and resemble a quantum hall effect, and in some limits support a quantized spin hall effect.[9] These materials have great implications for technology and topologically protected quantum computing. A more complex and sought after materials would be a topological superconductor. "Such a material would, aside from its fundamental interest by virtue of non-Abelian statistics, offer a new path to quantum computation,".[9]

Another intriguing material, and the focus of my research, is the QSL. One central question for physicists is to distinguish a spin-solid from a spin-liquid. If you take a snapshot, the ordering of the electrons spins appears the same for the two phases. However, by taking a "movie" through the process of neutron scattering (done at national facilities such as Oak Ridge), one can measure the spatial and time dependence of the spin-spin correlations, and the existence of a spin-liquid can be confirmed. Examples of QSLs have been demonstrated to exist on some geometrically frustrated magnets.[10] Some structure, such as the triangular lattice or the more complex kagomé lattice, tend to prefer the unordered ground state.[6]

Perhaps most intriguing and mysterious are gapless spin liquids. Topological order can be defined rigorously in states with an energy gap above the subspace of ground states. The type of order in a gapless spin liquid is harder to define, but there are explicit examples of models with gapless spin liquid ground states. A famous example on the honeycomb lattice was introduced by Kitaev113 and has been used as a basis for understanding inelastic neutron scattering on $RuCl_3$ (ref. 114). Even the kagomé lattice antiferromagnet may actually be a gapless state according to the most recent numerics, which shows how even simple Hamiltonians can host competing topological orders of various types.[9]

Through investigation of antiferromagnetic frustration and the QSL phase, many more exotic phases of matter are often discovered.[9] To better understand and control the competing and coexisting interactions in condensed materials, these exotic phases must first be shown to exist in real materials. Therefore, material discovery is an integral component of researching quantum materials.

1.3 Synthesis and Characterization

Another important aspect of experimental condensed matter physics is creating the materials to study. In his paper analyzing the discovery of quantum materials from a synthesis perspective, Nitin Samarth writes, "the rise of quantum materials in the contemporary sense of the term is a direct result of crystal growers effectively navigating toward materials that enable an emergent interplay between quantum confinement, topology, interactions, quantum fluctuations and quantum coherence,".[12] However, chemical synthesis is difficult, and many experiments require samples of complicated structure–whether it be bulk crystals, thin films, or nanostructure–in order to obtain the desired physical responses. Samarth discusses the most current methods used to synthesize desired structures and force desired physical properties in a material, expanding on topics of quantum confinement, topology by design, the role of disorder, and heterogeneous interfaces.[12]

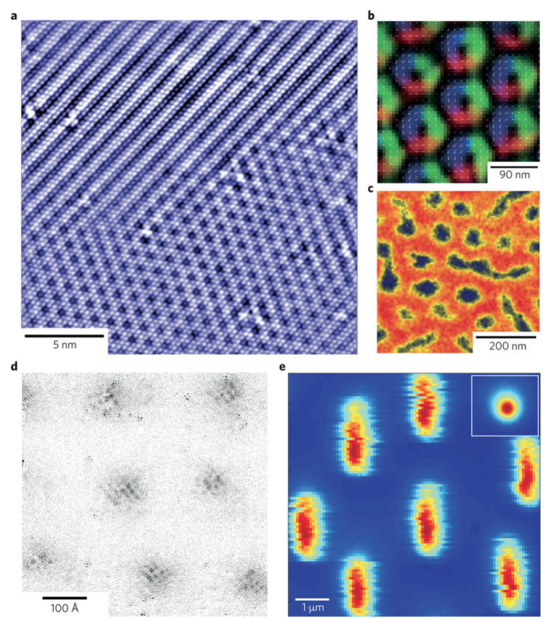

Figure 2: From Moler's recent paper,[11] these images reveal physical peoperties of materials at nanoscale lengths through many different imaging techniques. **a)** Scanning tunnelling microscope topography. **b)** Lorentz transmission electron microscopy. **c)**, **e)** Magnetic force microscopy. **d)** Scanning tunnelling spectroscopy.

Proper characterization of the material created is important to confirm that the structure which was synthesized is, in fact, the structure that was desired. Characterization is dependent on the quality of technology used, and recent progresses have allowed physicists to collect much more highly resolved data than ever before. In her recent paper, Moler discusses the "specialized imaging methods [that] are now available to measure the quantum properties of materials with high sensitivity and resolution. These techniques are key to the design, synthesis and understanding of materials with exotic functionalities,".[11] Various imaging techniques can reveal the collective phenomena of electrons in the quantum materials in different ways if the imaging techniques are elastic or inelastic and depending on the energy scales used (see Figure 2). My research focuses on imaging with x-ray backscattering and neutron scattering with an applied magnetic field.

In addition to the imaging techniques outlined by Moler, angle-resolved photoemission spectroscopy (ARPES) has recently been used to understand electronic structures of quantum materials, relying on the photoelectric effect to establish a relationship between the crystal momentum and binding energy inside of a solid.[13] With improved technology and imaging and analysis methods, physicists have begun to understand the nanoscale structural impacts on quantum behaviors.

1.4 Technological Applications

In their recent paper, Yoshinori Sensei, Masashi Kawasaki, and Naoto Nagaosa discuss the emergent functions that arise in quantum materials due to their physical properties.[14] These functions would enable topological electronics, quantum computation, above-RT superconductivity, and Mottronics, which would greatly affect modern technology (Figure 3).

In another paper, Basov, Averitt, Hsieh explain how these emergent functions can be produced on-demand in quantum materials.[15] The methods outlined in Basov's paper are numerous and utilize the many external stimuli detailed by Tokura (Figure 3b). The following are a few of the many ways and means of quantum control investigated in Basov's paper: static external perturbations, heterostructuring, applying high magnetic fields, high electric field perturbation and stimulation, nonlinear photonics, metastable states, polaritons, direct hopping modulation and Floquet engineering, as well as valley control and Berry phase modulation.[15] It is the ultimate goal of condensed matter physicists to 1) understand completely the physical behaviors of these exotic systems and 2) learn how to control these behaviors in order to produce desired effects with practical technological purposes. Therefore, the properties-on-demand approach (Figure 4) is crucial to the field of quantum materials in order to enable the many desired technological advances outlined by Yoshinori and the D.O.E..[8,14]

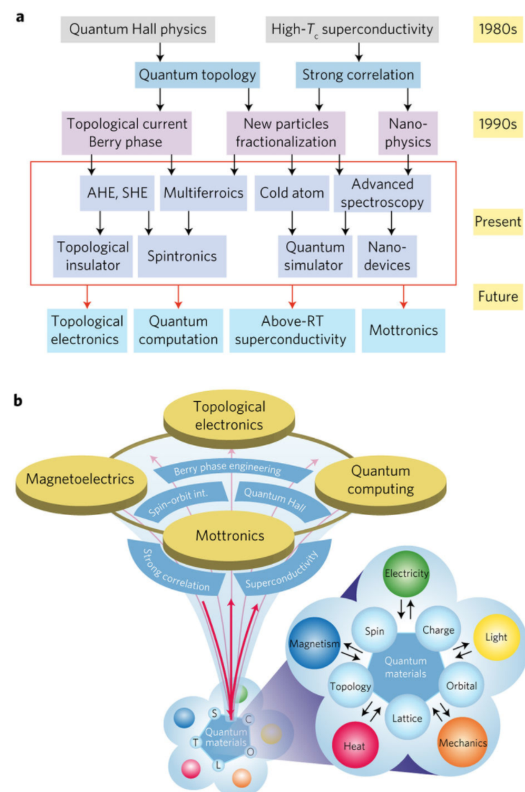

Figure 3: From Yoshinori's recent paper.[14] **a)** A brief history of research on the physics of quantum materials. **b)** A diagram relating the emergent functions (top) that arise in materials with strongly correlated electrons. The electrons' degrees of freedom (bottom) respond to various external stimuli (middle, right).

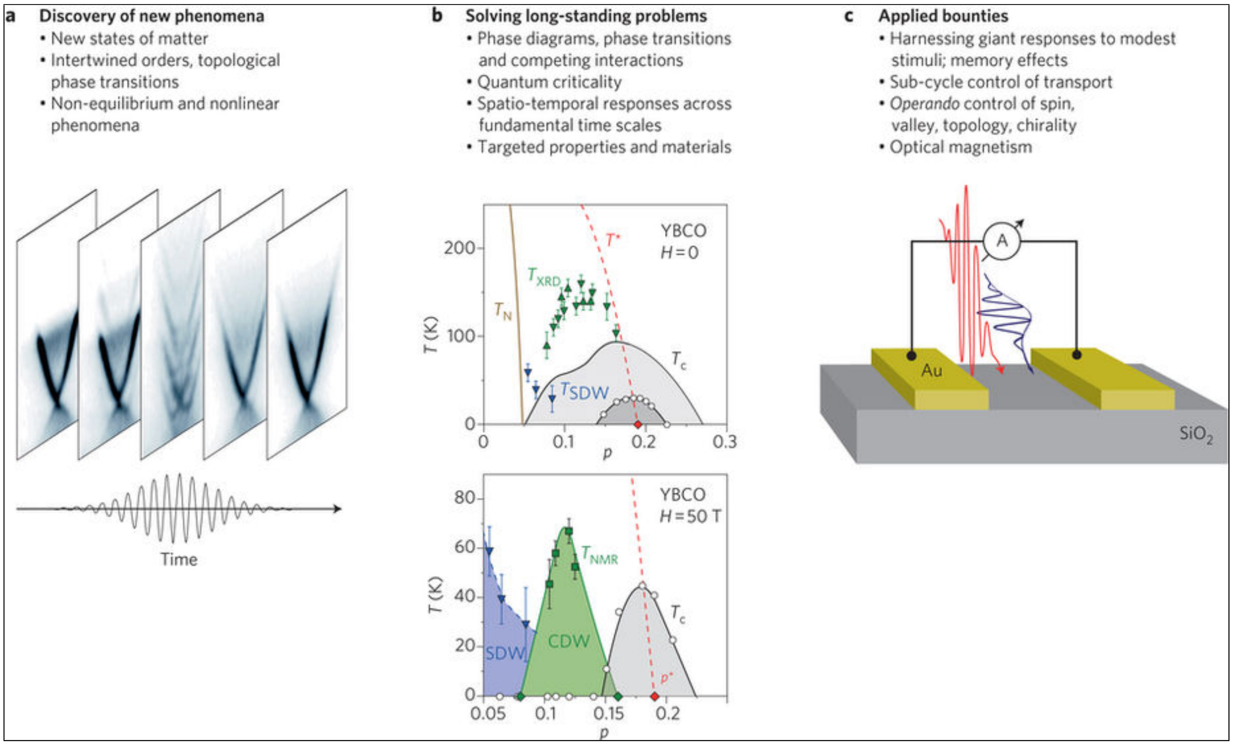

Figure 4: From Basov's recent paper, this figure demonstrates the properties-on-demand approach toward quantum materials.

Chapter 2

Triangular-Lattice Antiferromagnets

2.1 Forward

In this project, we studied two triangular-lattice frustrated magnets (Li-TAFs), Li_4CoTeO_6 and Li_4NiTeO_6. In these materials, Co and Ni ions with effective spin-$\frac{1}{2}$ and spin-1, respectively, each occupy the vertex points on the triangular lattice (Figure 5). These materials are of interest, because preliminary specific heat and isothermal magnetization measurements indicate a possible exotic magnetic ground state. Due to the triangular geometry, we expect to observe a QSL phase. The goal of this project is to understand the nature of the electron correlations down to near absolute-zero temperatures and determine the magnetic ground state of our materials.

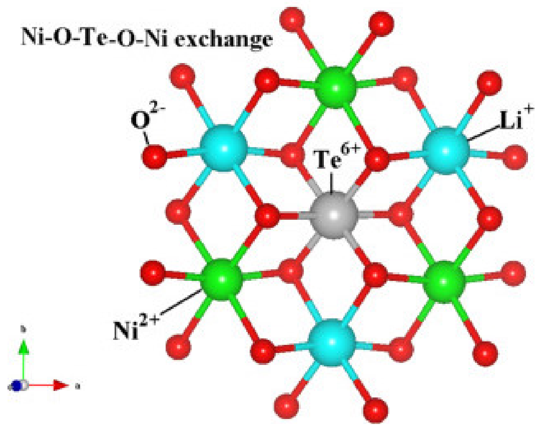

Figure 5: A cross-section of the Li_4CoTeO_6 and Li_4NiTeO_6 crystal structure.[16]

2.2 Sample Preparation

The samples used in this work were provided by our collaborator, Haidong Zhou from the Univeristy of Tennessee, Knoxville. The samples were powder and required certain preparations before measurements could be made.

To perform susceptibility measurements, we require a mixture of sample with silver (Ag) powder. Samples were ground into a fine powder, and powder Ag was added to increase the samples' thermal conductivity, accounting for about half of the combined sample mass. The powder combination was then placed in the pellet press in Mourigal's lab (Figure 6a), and a 1mm thick pellet was created for each material (Figure 6b and c). For magnetization measurements, Ag was not added, but the samples were still similarly ground to ensure uniform density.

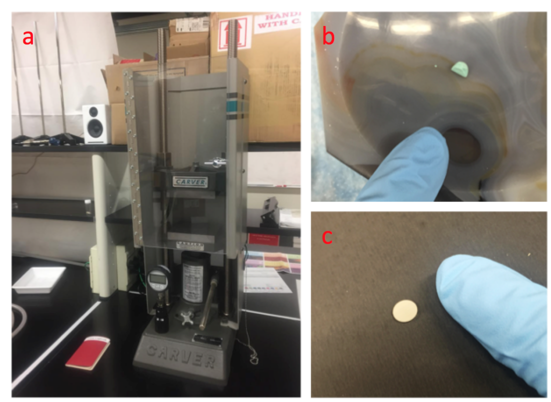

Figure 6: **a)** Pellet press in the Mourigal Lab. **b)** Unprepared powder sample of Li_4NiTeO_6. **c)** Prepared and pressed sample of Li_4CoTeO_6 + Ag combination.

2.3 Thermodynamic and Magnetization Measurements

To understand the physical properties of our materials, we conducted a range of thermomagnetic measurements:
(i) specific heat measurements at fixed magnetic field and varying temperature, down to 0.05 K;

(ii) susceptibility measurements at fixed magnetic field and varying temperature, down to 0.05 K; (iii) and isothermal magnetization measurements, up to 14 T.

All these measurements were conducted using the Quantum Design Dynacool Physical Property Measurement System (PPMS) in the Mourigal lab. The PPMS is equipped with a 14T magnet and can reach temperatures as low as 1.7 K. With an attached Quantum Design Dilution Refrigerator/Heat Capacity Capability Kit (DRHC), the PPMS can reach temperatures as low as 0.05 K.

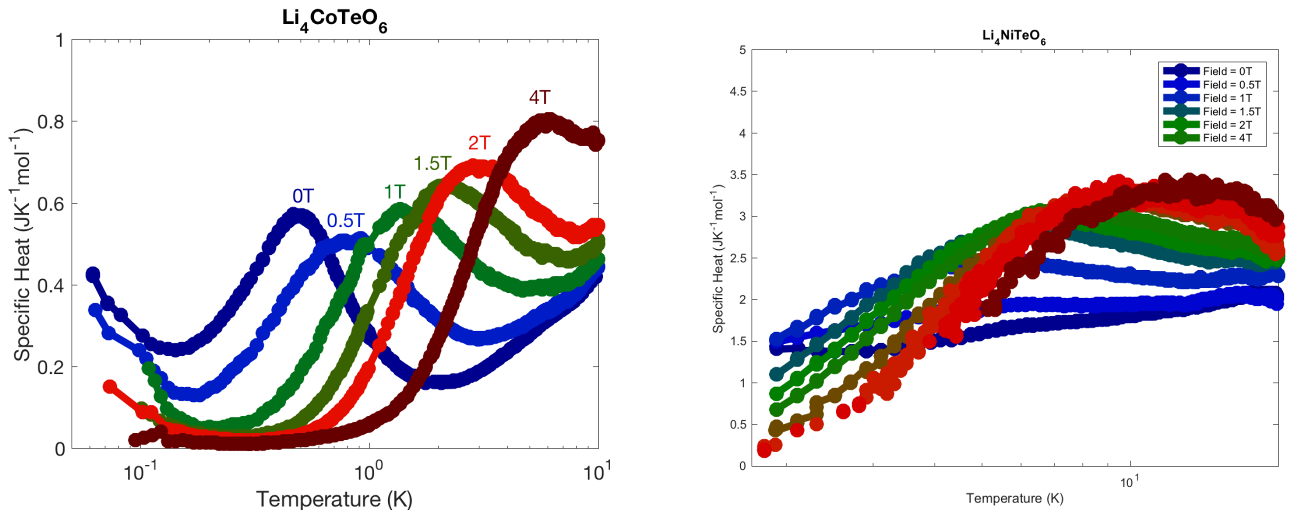

Figure 7: Heat capacity and susceptibility measurements for the Li_4CoTeO_6 sample (left) and the Li_4NiTeO_6 sample (right).

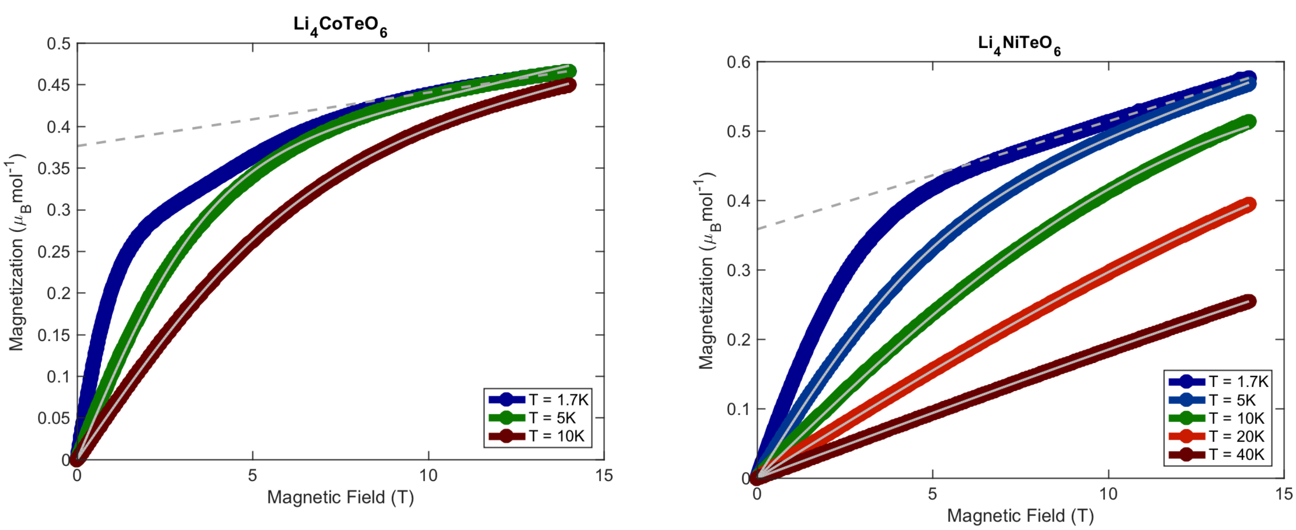

Figure 8: Magnetization measurements for the Li_4CoTeO_6 sample (left) and the Li_4NiTeO_6 sample (right).

For the heat capacity measurements, the relaxation method on the PPMS was used. Contributions from the Ag and from the sample platform were subsequently removed from the data, resulting in the following curves (Figures 7 and 8 for Li_4CoTeO_6 and Li_4NiTeO_6, respectively).

For the isothermal magnetization measurements, the sample was mounted in the Quantum Design Vibrating Sample Magnetometer (VSM) in the PPMS. The VSM vibrates the sample in the applied magnetic field and simultaneously measures the voltage induced in a nearby detection coil. This method produces magnetization curves with respect to the applied magnetic field, at a given temperature (shown in Figure 9 for the Li_4CoTeO_6 (left) and Li_4NiTeO_6 (right) samples).

Preliminary measurements of the specific heat versus temperature (Figure 7) and isothermal magnetization versus temperature (Figure 8) give a strong indication for a QSL phase on both materials.

2.4 X-ray and Neutron Scattering

With our evidence for a QSL phase in our Li-TAF materials, Mourigal and I co-authored a neutron scattering proposal to Oak Ridge National Lab. The proposal was accepted for the HFIR beamline, and elastic neutron scattering measurements were performed on samples prepared by Haidong Zhou. Additionally, x-ray scattering measurements were performed on our powder samples using the Empyrean X-ray Diffractometer at the Georgia Tech IEN/IMAT Materials Characterization Facility. The x-ray diffraction data and neutron scattering data were plotted for each sample, and agree with each other well (Figures 9 and 10).

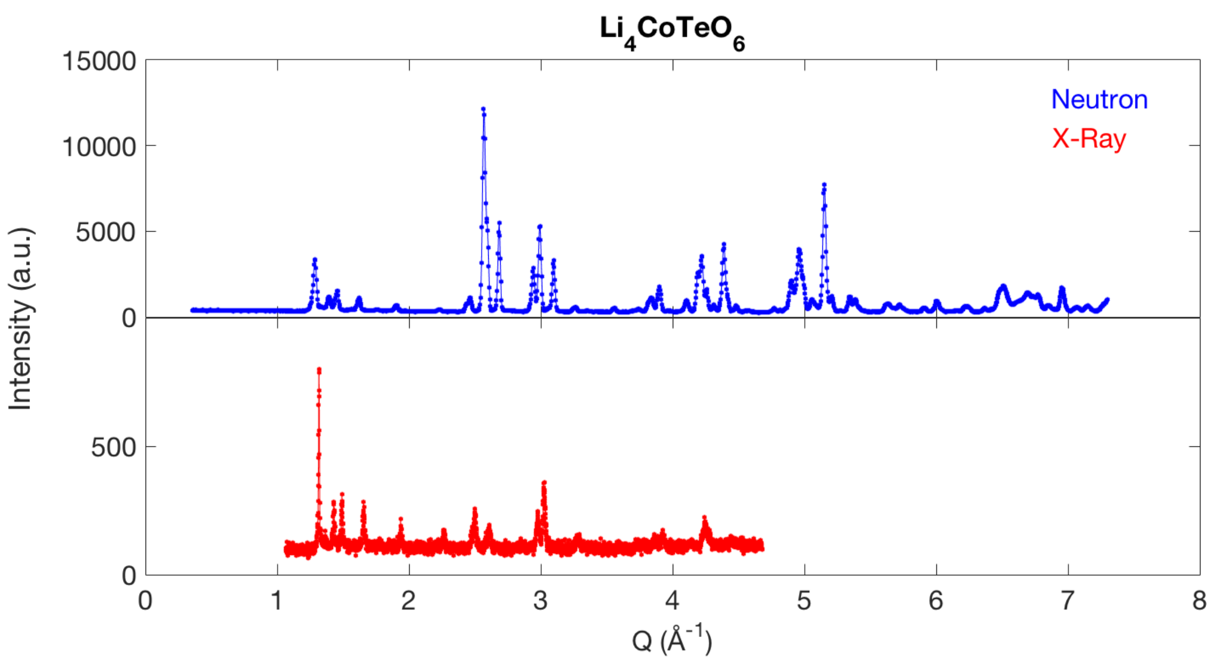

Figure 9: X-ray and neutron scattering data for the Li_4CoTeO_6.

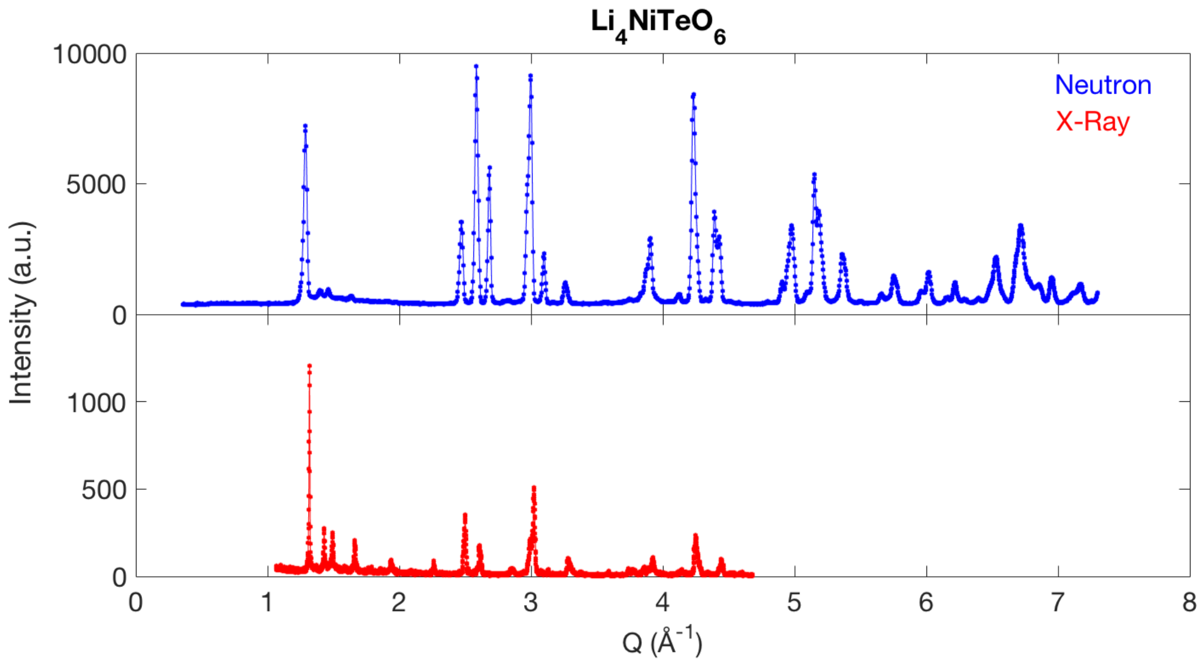

Figure 10: X-ray and neutron scattering data for the Li_4NiTeO_6.

2.5 Conclusion and Future Work

For our Li_4CoTeO_6 sample, we see a very interesting feature in the specific heat curve. At a very low temperature (approximately 0.5 K) there is a peak in specific heat versus temperature, indicative of a QSL phase change. This peak is not very sharp, however, and can indicate interesting magnetic behaviors down to 0 K temperatures. Additionally, we see a large deviation in the magnetization curve from the classical model, which provides more evidence for the QSL phase change. Due to these two features, we believe Li_4CoTeO_6 is a good candidate for the QSL phase, yet more measurements are still needed to determine this.

Neutron scattering measurements show no magnetic diffraction down to 0.1 K for Li_4CoTeO_6. However, susceptibility measurements show dominant anti-ferromagnetic interactions, due to its negative Currie-Weiss constant. Thus, we do not know if Li_4CoTeO_6 displays short-range order or a QSL phase. To determine this, we must perform inelastic neutron scattering to further probe the nature of the magnetic correlations.

For our Li_4NiTeO_6 sample, we also see an interesting feature in the specific heat curve. At low temperatures, there appears to be a broad peak in specific heat. With an applied magnetic field, though, this peak is broadened and observed a higher temperatures (approximately 5 K). With current data, we cannot resolve the true specific heat peak in the absence of a magnetic field. Additionally, we only see slight variations in the magnetization curve from the classical model, though variations do exist at temperatures as low as 1.7 K. Future work with this sample would involve measuring our sample with the DRHC down to 0.5 K to further understand the low temperature specific heat of our sample, as well as to perform inelastic neutron scattering measurements.

Chapter 3

Kagomé Lattice Antiferromagnets

3.1 Forward

In this project, we synthesized and studied the physical and magnetic properties of a popular kagomé lattice material (Figure 11), Fe-Jarosite ($KFe_3(OH)_6(SO_4)_2$). The spin dynamics[1] in Fe-Jarosite has not been investigated with modern neutron scattering tools and there is strong interest from the physics community to revisit this problem:[2] this is our first objective. Neutron scattering is the primary expertise in the Mourigal Lab (Physics). However, we run into the issue that scattering is weak. Because of this, large samples of Fe-Jarosite are needed to collect data with sufficient statistics. There is some difficulty in creating large single-crystalline samples of kagomé lattice materials, though.

For this project, we have teamed up with graduate student Ningxin Jiang in the LaPierre Lab (Chemistry department at Georgia Tech) to perform the synthesis. While making Fe-Jarosite, the La Pierre's group became interested in synthesizing novel materials with the Jarosite structure, by replacing Fe (3d-element) with various rare-earth ions (4f-elements) such as Yb or Er. Due to spin-orbit coupling, rare-earth elements carry spatially anisotropic magnetic moments that can lead to exotic physics.[10]

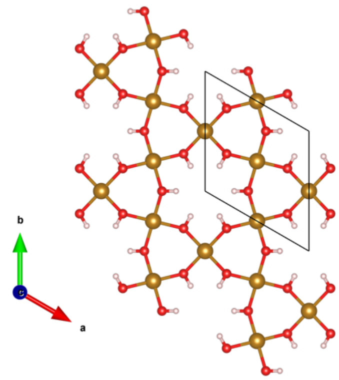

Figure 11: A cross-section of the Fe-Jarosite crystal structure.[1]

Figure 12: From the top: Parr hydrothermal vessels; multiple samples of Fe-Jarosite synthesized; one single crystal, 0.103in in length.

3.2 Material Synthesis and Characterization

The collaboration with graduate student Ningxin Jiang in the La Pierre Lab was aimed at creating and characterizing Fe-Jarosite crystals. Synthesis of Fe-Jarosite followed Daniel Nocera's methods[1,3] using Parr hydrothermal vessels with good results (Figure 12).

3.3 Magnetic Measurements

To search for QSL state in the newly prepared materials, we measured the isothermal magnetization of our sample versus temperature. This measurement was conducted using the Quantum Design Dynacool Physical Property Measurement System (PPMS) in the

Mourigal lab. The PPMS is equipped with a 14T magnet and can reach temperatures as low as 1.7 K. Preliminary measurements of the isothermal magnetization versus temperature (Figure 13) have been taken for one of our samples (single crystal pictured in Figure 12). Our results were found to be in good agreement with previous measurements for Fe-Jarosite crystals.[1,3]

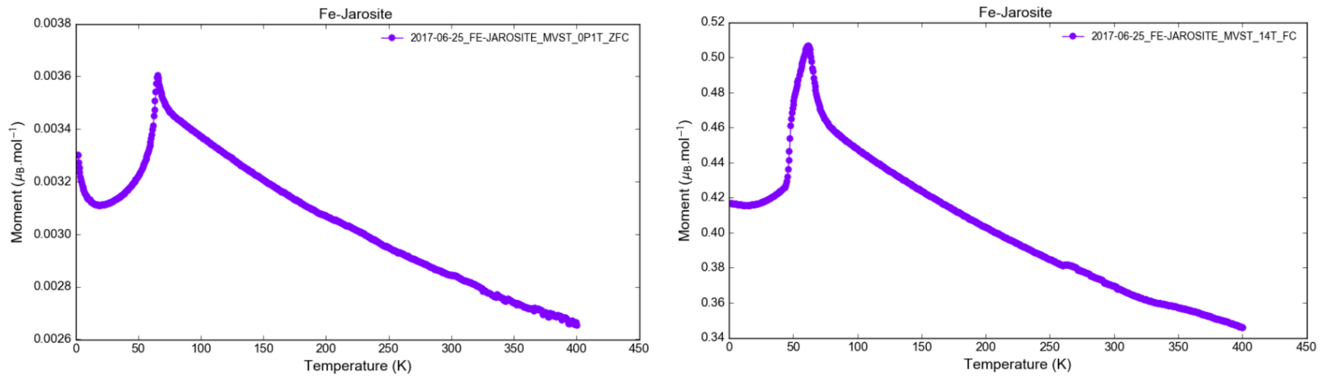

Figure 13: Isothermal Magnetization versus temperature measured for Fe-Jarosite at 0.1 T applied external magnetic field (left) and 14 T applied external magnetic field (right).

3.4 Conclusion and Future Work

Our synthesis efforts have been successful, but with only limited results (Figure 12). Future work would be to improve our synthesis techniques and create a large single crystal sample. Once large enough crystals are made, characterization of the crystals and their structure will be performed using the Empyrean X-Ray Diffractometer in the IEN/IMat Characterization Facility and the single-crystal X-ray diffractometer in the La Pierre's lab. Additionally, future work will be to perform neutron scattering experiments at large-scale national facilities, such as Oak Ridge National Lab, to better resolve the magnetic properties of this material.

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